



# Sandwiched SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> as a coke resistant nanocatalyst for dry reforming of methane

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## ABSTRACT

Design active and coke resistant Ni based catalysts is critical for implementation of dry reforming of methane technology. In this work, coke resistant SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst has been successfully prepared through precipitation of nickel nitrate with ammonia onto silica spheres, followed by coating with porous ZrO<sub>2</sub> shell. Through thermal treatment in air and hydrogen, nickel nanoparticles with size of 6 nm were sandwiched between silica core and zirconia shell. The ZrO<sub>2</sub> coated Ni catalyst exhibited a high activity of ~13.0 mol CH<sub>4</sub> per gram of Ni per hour for methane dry reforming at 700 °C, which is more than 6 times higher than that of SiO<sub>2</sub>@Ni catalyst under the same reaction condition. The SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst is also coke resistant as no carbon formation was observed for methane dry reforming at 700 °C for 20 h. As a comparison, carbon nanotubes formed over SiO<sub>2</sub>@Ni catalyst during dry reforming reaction with a coking rate of 0.019 g of carbon formed per gram of catalyst per hour. Operando XANES/EXAFS study of SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst confirmed metallic Ni phase during methane dry reforming from 400 to 800 °C. Theoretical calculations suggests that ZrO<sub>2</sub> stabilized Ni clusters lowers the highest dissociation energy barrier of CH<sub>4</sub> and CO<sub>2</sub> by 1.37 and 2.56 eV comparing to bulk Ni, increasing dry reforming activity on SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst. Furthermore, the higher binding energy of CO<sub>2</sub> over CH<sub>4</sub> on SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> leads to enrichment of CO<sub>2</sub> on catalyst surface, which mitigates coke formation.

## 1. Introduction

Dry reforming of methane (DRM) with carbon dioxide is a promising reaction to utilize methane from surplus natural gas supply to produce syngas, which is the important chemical intermediate for Fischer-Tropsch synthesis and methanol synthesis [1,2]. The syngas produced from DRM reaction with a relatively low H<sub>2</sub>/CO ratio is an ideal feedstock to be blended with stream from steam reforming of methane to adjust the ratio of H<sub>2</sub>/CO mixture for Fischer-Tropsch synthesis and methanol synthesis [3–7]. Furthermore, DRM reaction converts the greenhouse gas, CO<sub>2</sub> to valuable chemicals and mitigates emission of CO<sub>2</sub> to environment [8–10].

Nickel based catalysts have been widely used for DRM reaction due to their catalytic activities comparable to noble metal catalysts [11–15]. However, many of these Ni based catalysts undergo severe deactivation because of coke deposition via methane decomposition (CH<sub>4</sub> → C(s) + 2H<sub>2</sub>) and CO disproportionation (Boudouard reaction: 2CO →

C(s) + CO<sub>2</sub>) [16,17]. Sintering of nickel nanoparticles at high temperature during dry reforming of methane reaction is another challenge factor [18]. Other than reducing the exposed surface area of Ni, it further aggravates coke deposition when the size of Ni nanoparticles becomes larger.

Extensive efforts have been devoted to develop stable and coke resistant Ni catalysts for DRM reaction [19–27]. For example, molecular layer deposition (MLD) method has been applied to coat supported Ni nanoparticles with porous alumina film [3]. The coated porous alumina shell significantly enhanced the stability of Ni nanoparticles. Coating of nickel nanoparticles with porous shell has also been achieved using wet chemistry synthesis method [28–32]. Generally Nickel nanocrystals were prepared first, followed by coating with porous silica shell. The resulted core-shell nanocatalysts exhibit excellent performance for dry reforming reaction [8]. However, it is known that the structural stability of porous silica materials is a concern at high temperature in the presence of steam [33,34]. As water is the byproduct of reforming

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reaction due to reverse water gas shift reaction, the long term stability of porous silica shell needs to be addressed.

In this work, nickel doped silica spheres ( $\text{SiO}_2@\text{Ni}$ ) was prepared via so-gel synthesis of in ethanol solution (Fig. S1). The synthesized  $\text{SiO}_2@\text{Ni}$  spheres were then used as the core material for coating with porous zirconia shell. Finally, the formed  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  sample was thermally treated to decompose the organic template. The structure, morphology, and reducibility of the as-synthesized catalysts were characterized by XRD, TEM/EDX, and TPR. The prepared  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  catalysts have been investigated for methane dry reforming reaction at 200–900 °C, and the catalytic activity was measured based on methane conversion. The activation energies of  $\text{CH}_4$  and  $\text{CO}_2$  were determined for  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  catalysts from kinetic study. Coke resistance of the Ni catalysts with or without  $\text{ZrO}_2$  coating was studied by examining the spent catalysts. Furthermore, computational studies were performed to understand the mechanism of methane dry reforming on Ni catalysts.

## 2. Experimental section

### 2.1. Synthesis of $\text{SiO}_2@\text{Ni}$ spheres

In a typical synthesis, 1 mL of tetraethyl orthosilicate (TEOS, Acros, 98%) was added to 20 mL of ethanol (Fisher Chemical, HPLC grade), followed by adding 2 mL of ammonia solution ( $\text{NH}_4\text{OH}$ , Sigma-Aldrich, 28.0–30.0%). The resulted mixture was stirred at room temperature for 1 h. After that, 2.3 mL of 0.2 M nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Fisher Chemical, Certified grade) solution was added to above mixture, and was stirred at room temperature for 10 min. The product was collected by centrifugation, and was washed with ethanol for 3 times.

### 2.2. Preparation of $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$ core-shell nanocatalysts

The product collected above was re-dispersed in 20 mL of ethanol, followed by adding 0.1 mL of water and 0.1 mL of brij 30 ( $\text{C}_{20}\text{H}_{42}\text{O}_5$ , Acros). The resulted mixture was stirred for 30 min, followed by adding 0.2 mL of zirconium n-butoxide ( $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Zr}$ , Alfa Aesar, 80% w/w in 1-butanol). The resulted mixture was further stirred at room temperature for 16 h. The product was centrifuge and re-disperse in 20 mL of water for 1 day. The product was collected by centrifuge and washed with water for 3 times, followed by drying at 70 °C overnight. After that, the as-synthesized  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  were calcined in static air at 550 °C for 3 h, and were named as calcined  $\text{SiO}_2@\text{Ni}$  and calcined  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$ , respectively. The calcined samples were further reduced in 10%  $\text{H}_2/\text{N}_2$  at 700 °C for 1 h, and were named as reduced  $\text{SiO}_2@\text{Ni}$  and reduced  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  accordingly (or simply as  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$ ).

### 2.3. Characterization

The crystallographic structure of prepared  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@Z\text{rO}_2$  catalysts were studied by powder X-ray diffraction (XRD, Rigaku Ultima III,  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.54059 \text{ \AA}$ ) at a scanning rate of 2°/min. The morphology and chemical composition of the nanocatalysts were characterized with transmission electron microscopy coupled with energy dispersive X-ray spectroscopy (TEM/EDX, JEOL JEM-2100). The specific surface area of the core-shell catalysts was determined using  $\text{N}_2$  adsorption and desorption analysis (Quantachrome Autosorb-1). The reducibility of nickel catalysts were examined with  $\text{H}_2$  temperature programmed reduction ( $\text{H}_2$ -TPR, Quantachrome ChemBET Pulsar TPR/TPD). The content of Ni was determined by EDX mapping using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX, Zeiss, EVO 50), with average of five measurements for each sample. The coke deposition on catalyst after dry reforming reaction was analyzed with thermogravimetric method (TGA, Shimadzu, TGA-50).

### 2.4. Operando X-ray absorption spectroscopy (XAS)

Operando XAS measurement of Ni K edge of nickel catalyst under reduction and reaction conditions was carried out on the bending magnet beamline 9-BM-C at the Advanced Photon Source (APS) within Argonne National Laboratory. The data was collected in transmission step-scan mode. Photon energies were selected with a double crystal Si (111) monochromator, and harmonic rejection was achieved using a rhodium coated flat mirror. The ionization chambers were optimized for 10% absorption in the incident ion chamber and 70% absorption in the X-ray detector. Ni foil standard was placed downstream of the sample cell as a reference to calibrate the photon energy of each measured spectrum. The catalyst sample was pressed as a self-supporting wafer into a cylindrical sample holder having six holes. The sample thickness was chosen to give a total absorbance ( $\mu\text{x}$ ) at Ni K-edge between 1 and 2, and edge steps ( $\Delta\mu\text{x}$ ) around 0.3–0.5. The sample holder was inserted into a quartz tube reactor, which was heated by a horizontal cylindrical furnace. Continuous measurement of Ni K-edge of the catalyst was carried out under reduction and reaction conditions. The catalyst was heated from room temperature to 700 °C at 5 °C/min in the presence of 100 mL/min of 3.5%  $\text{H}_2/\text{He}$  gas flow. After reduction, the reactor was cooled to 400 °C in 100 mL/min of  $\text{N}_2$  flow. Then, the gas was switched to 5%  $\text{CH}_4/5\%\text{CO}_2/90\%\text{N}_2$ , and the reactor was heated from 400 to 800 °C step wisely with the interval of 100 °C. At every reaction temperature (i.e., 400, 500, 600, 700, and 800 °C), the DRM reaction was allowed to proceed for 1 h with continuous measuring Ni K-edge. The measured XANES/EXAFS spectra was processed and fitted with IFEFFIT using Athena and Artemis programs [35,36]. The edge energy was determined from the first inflection point on the rising edge of the XANES spectra. Background subtraction was carried out using Autobk and Spline smoothing functions in the Athena program. The k-range and R-range used for the fittings are 3–13  $\text{\AA}^{-1}$  and 1–5.4  $\text{\AA}$ , respectively.

### 2.5. Dry reforming of methane with carbon dioxide

The methane dry reforming reaction was carried out at atmospheric pressure using a tubular quartz fixed bed reactor with inner diameter of 6 mm. In a typical experiment, 50 mg of catalysts with size of 40–60 mesh was packed into the center of the reactor using quartz wool. The thermocouple was inserted into the reactor and closed to the catalyst bed. Before reaction, the catalyst was reduced at 700 °C for 1 h in 10%  $\text{H}_2/\text{N}_2$  gas mixture with a flow rate of 100 mL/min. After reduction, the inlet gas was switched to reactant gas mixture of  $\text{CO}_2/\text{CH}_4/\text{N}_2$  (1:1:1) with a flow rate of 60 mL/min. For measuring activities at 200–900 °C, 20 mg of catalyst was used and the weight hourly space velocity (WHSV) was 180,000  $\text{ml g}^{-1} \text{h}^{-1}$ . The reaction was monitored with an online gas chromatograph (GC, Agilent 7890A) coupled with flame ionized detector (FID) and thermal conductive detector (TCD). The product gas mixture was separated using Hayesep Q and MolSieve 5A columns.

## 3. Computational details

### 3.1. Calculation methods

Density functional theory (DFT) calculations are performed by projector augmented wave (PAW) method in the Vienna Ab Initio Simulation Package (VASP) [37,38]. The spin-polarized Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional was employed for the exchange–correlation energy [39–41]. A cutoff energy is set to 400 eV. The geometry is optimized when the forces on atoms are less than 0.03 eV/ $\text{\AA}$ . The Brillouin zone is sampled by a k-point of  $3 \times 3 \times 1$  and Methfessel-Paxton smearing width is employed with 0.20 eV. The Ni bulk lattice constant and magnetic moment are calculated to be 3.524  $\text{\AA}$  and 1.63  $\mu\text{B}$  per atom, which accord well with

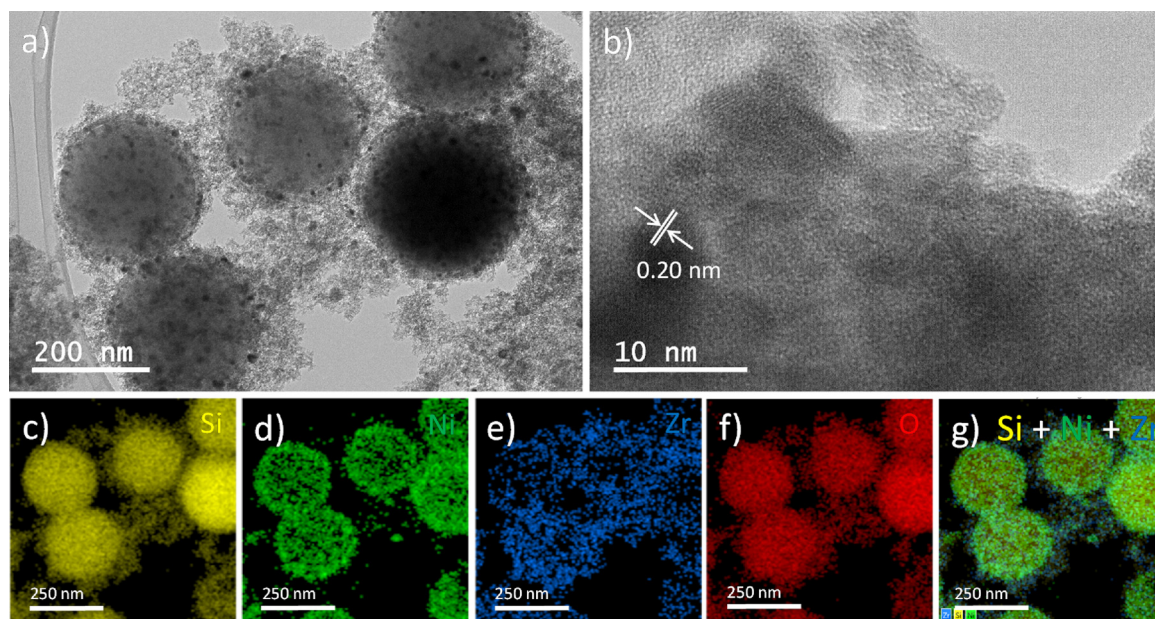


Fig. 1. (a, b) TEM images and (c–g) EDX mapping of reduced  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts.

the experimental values of  $3.523 \text{ \AA}$  and  $1.61 \mu\text{B}$ , respectively [42,43]. The Climbing-Image Nudged Elastic Band method (CI-NEB) is used to obtain the minimum energy path [44,45], which is inserted with at least four images between the initial and final states. The forces for all atoms in the transition state structures are less than  $0.05 \text{ eV/\AA}$ . Moreover, the van der Waals interaction was considered for the adsorption of  $\text{CH}_4$  and  $\text{CO}_2$  using the DFT-D2 method of Grimme [46]. In addition, the isolated atoms and gaseous molecules are optimized in a  $10 \times 10 \times 10 \text{ \AA}$  cubic cell.

### 3.2. Calculation model

To simulate the large Ni nanoparticles in  $\text{SiO}_2@\text{Ni}$  catalyst, the close-packed Ni(111) surface with the dominantly exposed facet of face-centered cubic (FCC) metals is selected as the catalyst model. As shown in Fig. S7(a), the  $p(3 \times 3)$  unit cell is cleaved with the slab thickness of four-layers, in which the top three layers and adsorbed species are allowed to relax, while the bottom layers are fixed in their bulk position. The vacuum thickness of  $15 \text{ \AA}$  between the repeated slabs can be maintained to exclude the slab interactions. Four adsorption sites exist: top, bridge, hcp and fcc sites (hcp and fcc are the 3-fold hollow site).

On the other hand, for the model construction of the small Ni nanoparticle in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst based on the following reasons, firstly, TEM results show metallic Ni in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst largely exposed the (111) plane (see the 1<sup>st</sup> paragraph in Section 4.1); secondly, in situ EXAFS also confirmed the metallic state of Ni nanoparticles under reaction condition; thirdly, the Fourier transformed EXAFS spectra confirm the Ni-Ni distance of  $2.47 \text{ \AA}$  and the coordination number of 8.8 (see the 1<sup>st</sup> paragraph of Section 4.3); further, Ni nanoparticles with a size of  $\sim 6 \text{ nm}$  were built containing thousands of atoms, because of the large number of atoms, it is impossible for us to perform DFT calculations study on them. Thus, in this study, compared to the large Ni nanoparticle in  $\text{SiO}_2@\text{Ni}$  catalyst simulated by the periodic Ni(111) surface, the  $\text{Ni}_{15}$  cluster is built to qualitatively reflect the largely exposed (111) plane consisted of the 3-fold hollow site, which is also the dominant surface characteristic of the small Ni nanoparticle in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst. Moreover, as mentioned in this study, the calculated results using the  $\text{Ni}_{15}$  cluster can well describe the catalytic performance of the small Ni nanoparticle in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst. Therefore, based on the experimental characterizations by TEM and EXAFS, a  $\text{Ni}_{15}$  cluster is constructed to reflect the characteristic of the

small Ni nanoparticle in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst. As shown in Fig. S7(b), a  $\text{Ni}_{15}$  cluster is supported on an eight-layers  $p(2 \times 2)$   $\text{ZrO}_2(111)$  surface, where the top four layers together with the  $\text{Ni}_{15}$  cluster are relaxed, and the bottom four layers are fixed in their bulk positions. The slab is separated by  $20 \text{ \AA}$  vacuum to ensure the negligible interaction between the adsorbates and the slab. There are four types of adsorption sites: top, bridge, 3-fold hollow and 4-fold hollow sites, where the Ni atom serial number was labeled to easily locate the following adsorption site in the study.

## 4. Results and discussion

### 4.1. Synthesis and characterization of $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$ catalyst

The  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  core-shell nanocatalysts were prepared by a wet chemistry synthetic route. Silica spheres were synthesized by hydrolysis of TEOS in ethanol in the presence of ammonia. following a modified Stober method [47]. After forming silica spheres, nickel nitrate solution was added to the silica synthetic solution. The opaque solution turned light blue immediately due to precipitation of nickel nitrate with ammonia on the surface of silica spheres. The resulted  $\text{SiO}_2@\text{Ni}$  spheres were further coated with porous  $\text{ZrO}_2$  shell by hydrolysis of zirconium butoxide in water/ethanol mixture in the presence of surfactant [48]. The as-synthesized sample was further heated in air and hydrogen consecutively to burn off surfactant and reduce Ni to metallic state. The morphology of reduced  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst was examined by TEM. As shown in Fig. 1, the  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst exhibits a core-shell structure with size of around  $250 \text{ nm}$ . The surface of silica spheres is decorated with Ni nanoparticles, which has a size of  $\sim 6 \text{ nm}$ . The lattice spacing of  $0.20 \text{ nm}$  measured from the high resolution image can be assigned to (111) plane of cubic phase metallic Ni (JCPDS 04-0850). The Ni nanoparticles decorated silica spheres is covered with porous  $\text{ZrO}_2$  shell. The core-shell structure of  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  is further confirmed by EDX mapping. Shown in Fig. 1c–g, Most of the Ni nanoparticles are sandwiched between silica core and zirconia shell. It shows that porous  $\text{ZrO}_2$  shell is effective to stabilize  $6 \text{ nm}$  Ni nanoparticles, as the reduced  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst has been thermally treated at  $550^\circ\text{C}$  in air and  $700^\circ\text{C}$  in  $10\%\text{H}_2/\text{N}_2$ . It is noted that a few Ni nanoparticles are detached from the silica surface (Fig. 1d). By examining the region of detached Ni nanoparticles, both silica and zirconia also present in that area and encapsulate the Ni nanoparticles (Fig. 1c and



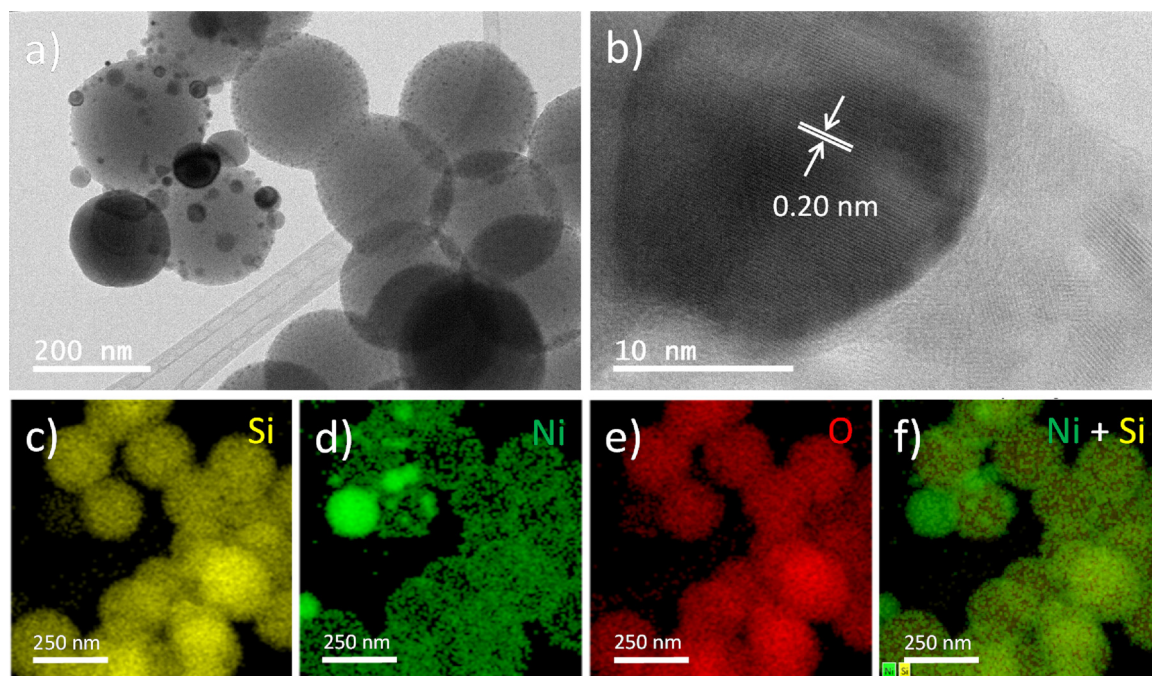


Fig. 2. (a, b) TEM images and (c–f) EDX mapping of reduced  $\text{SiO}_2@\text{Ni}$  catalysts.

e). Furthermore, from synthetic point of view, nickel was deposited onto silica surface in the presence of ammonia, which was then covered by zirconia. Without silica spheres core, precipitation of large nickel hydroxide particles is anticipated, eventually resulting in poor dispersion of Ni. As a comparison, the  $\text{SiO}_2@\text{Ni}$  catalyst without  $\text{ZrO}_2$  coating has also been examined by TEM (Fig. 2). Unlike  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  sample, Ni nanoparticles in  $\text{SiO}_2@\text{Ni}$  exhibits a bimodal size distribution. In addition to 6 nm Ni nanoparticles dispersed on the surface of  $\text{SiO}_2$  spheres, there are many large Ni particles observed with size as large as 170 nm. The presence of large Ni particle is due to sintering of Ni during thermal treatment, which further confirms the importance of  $\text{ZrO}_2$  shell for stabilizing small Ni nanoparticles.

The crystallographic structure of  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts were examined by powder X-ray diffraction (Fig. 3a). For  $\text{SiO}_2@\text{Ni}$ , three sharp peaks appear at  $44.4^\circ$ ,  $52.0^\circ$ , and  $76.5^\circ$ , which are attributed to (111), (200), and (220) plane of cubic metallic Ni phase (JCPDS 04-0850). The broad peak around  $21.2^\circ$  is due to amorphous silica spheres [49,50]. After coating with  $\text{ZrO}_2$ , only two small peaks for metallic Ni are observable at  $44.4^\circ$  and  $52.0^\circ$ . It is noted that Ni loading in  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  is 12.2 and 8.9%, respectively (Table 1). Thus the sharp decrease in the intensity of Ni peaks is most likely due to smaller Ni particles (e.g., 6 nm) in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  comparing to  $\text{SiO}_2@\text{Ni}$  catalyst. The average size of Ni particles in  $\text{SiO}_2@\text{Ni}$  and  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts is calculated to be 33.1 and 5.6 nm from

broadening of Ni(111) peak using Scherrer equation. As the size of Ni nanoparticles in  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  is quite uniform, the size determined from Scherrer equation is consistent with TEM observation.

Reducibility of calcined  $\text{SiO}_2@\text{Ni}$  and calcined  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  samples was studied by  $\text{H}_2$ -TPR (Fig. 3b). Two reduction peaks are observed at 388 and 580  $^\circ\text{C}$  for calcined  $\text{SiO}_2@\text{Ni}$  sample. The first peak at 388  $^\circ\text{C}$  could be assigned to big NiO particles on the surface of silica spheres, which is relatively easier to be reduced [23]. The second peak at higher temperature (i.e., 580  $^\circ\text{C}$ ) is attributed small NiO particles partially or fully covered by silica [51]. After coating with  $\text{ZrO}_2$ , there is only one reduction peak observed at 734  $^\circ\text{C}$ . It suggests there is strong interaction between surface NiO and  $\text{ZrO}_2$ , which stabilize Ni nanoparticles at high temperature. In the literature, a number of Ni/ $\text{ZrO}_2$  based catalysts have been reported for methane dry reforming reaction [52–58]. It is noted that the reduction peak of Ni/ $\text{ZrO}_2$  catalysts generally occurs at 490–550  $^\circ\text{C}$  [53,57]. For  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst, the reduction peak was observed at 734  $^\circ\text{C}$ , which is nearly 200  $^\circ\text{C}$  higher than those of Ni/ $\text{ZrO}_2$  catalysts. It is possibly attributed to the unique core-shell structure with Ni nanoparticles assembled between silica core and zirconia shell, resulting in strong interaction between Ni and support.

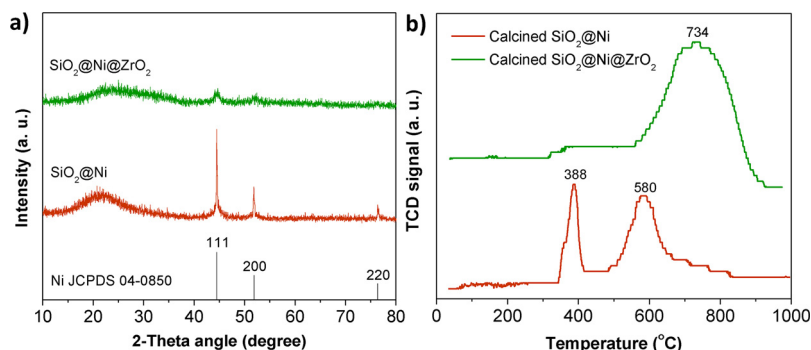


Fig. 3. (a) XRD patterns of reduced  $\text{SiO}_2@\text{Ni}$  and reduced  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts. (b)  $\text{H}_2$ -TPR of calcined  $\text{SiO}_2@\text{Ni}$  and calcined  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  samples.

**Table 1**Dry reforming of methane over SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalysts.<sup>a</sup>

Catalyst	Ni Content (%)	Surface area (m <sup>2</sup> /g)	Temperature (°C)	CH <sub>4</sub> Conversion (%)	CO <sub>2</sub> Conversion (%)	CO Selectivity (%)	H <sub>2</sub> /CO ratio	Activity (mol g <sup>-1</sup> h <sup>-1</sup> ) <sup>b</sup>
SiO <sub>2</sub> @Ni	12.2	195	500	1.3	0.4	–	–	0.28
			600	4.4	3.3	76.9	0.55	0.98
			700	9.1	7.6	88.2	0.57	1.99
			800	34.5	37.6	94.0	0.73	7.58
			900	83.4	81.5	94.7	0.95	18.31
SiO <sub>2</sub> @Ni@ZrO <sub>2</sub>	8.9	226	500	7.2	6.9	83.3	0.49	2.17
			600	16.3	19.0	90.3	0.54	4.90
			700	43.1	48.8	94.7	0.76	12.99
			800	79.2	80.6	95.2	0.95	23.84
			900	98.8	95.0	94.0	1.00	29.74
0.5Ni/CeNi <sub>x</sub> O <sub>y</sub> <sup>c</sup>	15.1	94	800	47.8	55.7	–	0.79	8.5
Ni <sub>15</sub> CeMgAl <sup>d</sup>	15.0	243	800	99	82	–	0.80	5.9

<sup>a</sup> Reaction condition: CH<sub>4</sub>:CO<sub>2</sub>:CO = 1:1:1, 20 mg of catalyst + 0.2 g quartz sand, WHSV = 180,000 mL g<sup>-1</sup> h<sup>-1</sup>, 500–800 °C, 1 bar.<sup>b</sup> Activity was calculated as mole of CH<sub>4</sub> converted per total gram of Ni per hour.<sup>c</sup> From ref. [23]. CH<sub>4</sub>:CO<sub>2</sub>:CO = 1:1:1, WHSV = 180,000 mL g<sup>-1</sup> h<sup>-1</sup>.<sup>d</sup> From ref. [9]. CH<sub>4</sub>:CO<sub>2</sub> = 1.04:1, GHSV = 48,000 h<sup>-1</sup>.

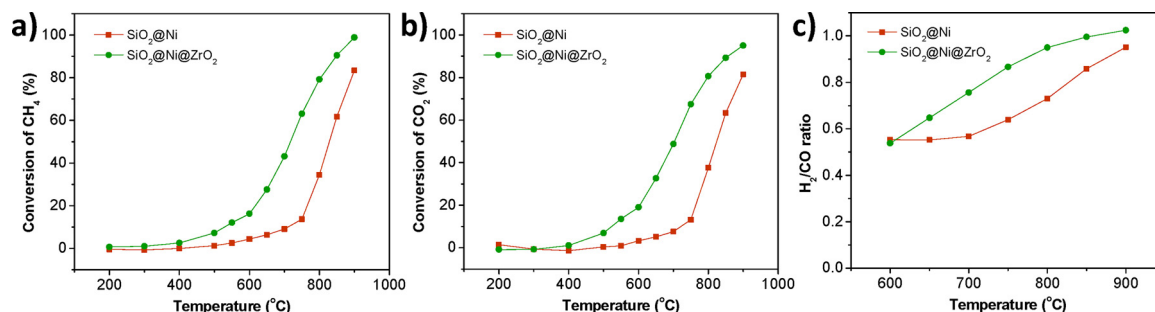
#### 4.2. Methane dry reforming over Ni core-shell catalysts

The reduced SiO<sub>2</sub>@Ni and SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalysts have been investigated for dry reforming of methane reaction at 200–900 °C (Fig. 4 and Fig. S3). For SiO<sub>2</sub>@Ni catalyst, the reaction starts at around 500 °C with conversion of CH<sub>4</sub> as 1.3 and 4.4% at 500 and 600 °C, respectively. The conversion of CH<sub>4</sub> increases to 9.1 and 34.5% at 700 and 800 °C accordingly. At 900 °C, the CH<sub>4</sub> conversion reaches 83.4%. Similarly, the initial conversion of CO<sub>2</sub> at below 600 °C is less than 5%. Increasing the reaction temperature to 700, 800 and 900 °C, the CO<sub>2</sub> conversion increases to 43.1, 79.2, and 98.8% at, respectively. By coating SiO<sub>2</sub>@Ni with ZrO<sub>2</sub> shell, the methane dry reforming activity improves significantly. At 500 °C, both of the conversions for CH<sub>4</sub> and CO<sub>2</sub> are higher than 5%, as 7.2 and 6.9% accordingly. The activity was calculated as mole of CH<sub>4</sub> formed per total gram of Ni per hour. The activity of SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst is 2.17 mol g<sup>-1</sup> h<sup>-1</sup> at 500 °C, which is 7 times higher than that of SiO<sub>2</sub>@Ni catalyst (0.28 mol g<sup>-1</sup> h<sup>-1</sup>). Increasing the reaction temperature to 600 and 700 °C, the CH<sub>4</sub> conversion increases to 16.3 and 43.1%, while the CO<sub>2</sub> conversion increases to 19.0 and 48.8%, respectively. The activity of SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst is 4.90 and 12.99 mol g<sup>-1</sup> h<sup>-1</sup> at 600 and 700 °C, which is 5–6 times higher than that of SiO<sub>2</sub>@Ni catalyst at the same reaction temperature. At 800 °C, the activity of SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst is 23.84 mol g<sup>-1</sup> h<sup>-1</sup>, which is about 2.8–4.0 times higher than previous reported 0.5Ni/CeNi<sub>x</sub>O<sub>y</sub> (8.5 mol g<sup>-1</sup> h<sup>-1</sup>) and Ni<sub>15</sub>CeMgAl (5.9 mol g<sup>-1</sup> h<sup>-1</sup>) catalysts under similar reaction conditions. At 900 °C, more than 95% conversion of CH<sub>4</sub> and CO<sub>2</sub> conversion is achieved for SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst. It was observed that the H<sub>2</sub>/CO ratio is less 1, which was attributed to the reaction between H<sub>2</sub> and CO<sub>2</sub> to generate H<sub>2</sub>O and CO via reverse water gas shift reaction, as suggested by the equilibrium profile of dry reforming reaction (Fig. S4).

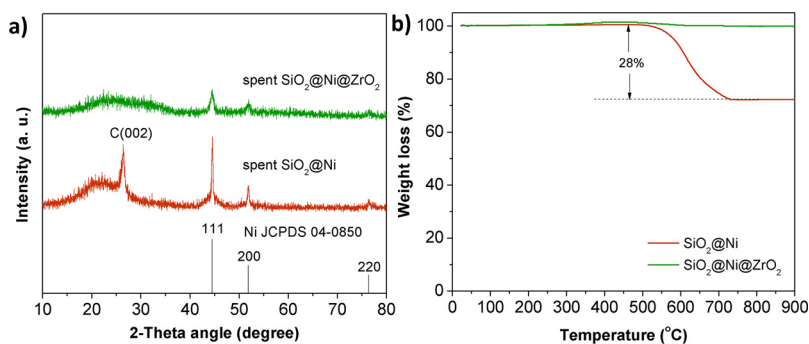
The coking resistance of SiO<sub>2</sub>@Ni and SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalysts were studied by examining the spent catalysts after dry reforming reaction at 700 °C for 20 h with a total flowrate of 60 mL/min (CH<sub>4</sub>:CO<sub>2</sub>:N<sub>2</sub> = 1:1:1). Fig. 5a presents the XRD patterns of spent SiO<sub>2</sub>@Ni and SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalysts. Similar as fresh catalysts, the peaks at 44.5, 51.8, and 76.5° are attributed to (111), (200), and (220) plane of metallic Ni. For spent SiO<sub>2</sub>@Ni catalyst, there is additional peak observed at 26.4°, which is assigned to (002) plane of graphitic carbon [59,60]. It shows that carbon was formed on SiO<sub>2</sub>@Ni catalyst during dry reforming reaction, either from decomposition of CH<sub>4</sub> and/or disproportionation of CO. However, there is no carbon peak in the XRD pattern for spent SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst, suggesting that SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> is a carbon resistant catalyst for dry reforming reaction. The coke resistance of SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> is attributed to porous ZrO<sub>2</sub> coating, which stabilize small Ni nanoparticles during thermal treatment and dry reforming reaction and inhibits carbon deposition on catalyst surface.

The amount of deposited carbon was analyzed by thermogravimetric experiment. The spent catalyst was heated in air up to 900 °C, and the weight change of catalyst was monitored continuously. Shown in Fig. 5b, there is no change of weight for spent SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst, further confirming that no carbon deposition on SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst during dry reforming reaction. On the contrary, there is weight loss observed from 500 to 730 °C for SiO<sub>2</sub>@Ni catalyst, which is attributed to burn off of graphitic carbon [61,62]. Based on the total weight loss of 28% for SiO<sub>2</sub>@Ni catalyst, the coking rate (defined as gram of carbon formed per gram of catalyst per hour) is calculated to be 0.019 g g<sup>-1</sup> h<sup>-1</sup>. It was noted that there was small amount (i.e., ~0.5–1.0 wt%) of weight gain at ~300–500 °C (Fig. 5b), possibly due to oxidation of supported nanoparticles to nickel oxide.

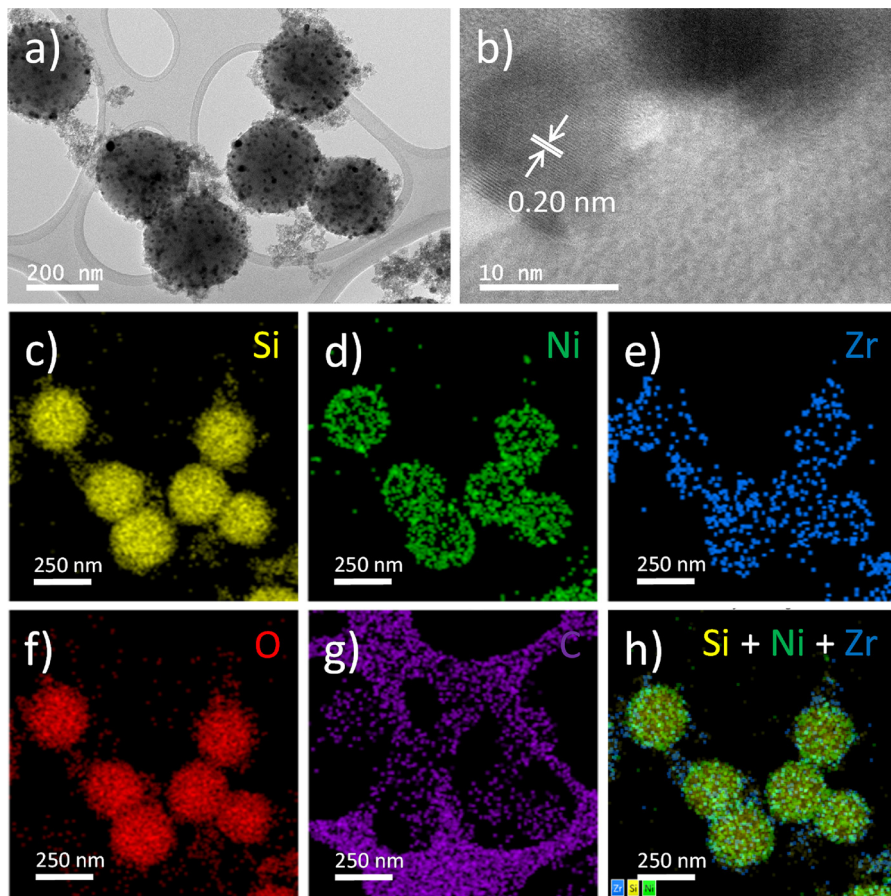
The spent catalysts were further characterized by TEM to examine



**Fig. 4.** Dry reforming of CH<sub>4</sub> with CO<sub>2</sub> over SiO<sub>2</sub>@Ni and SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalysts: (a) conversion of CH<sub>4</sub>, (b) conversion of CO<sub>2</sub>, and (c) H<sub>2</sub>/CO ratio. Reaction condition: 20 mg of catalyst + 0.2 g quartz sand, CH<sub>4</sub>:CO<sub>2</sub>:N<sub>2</sub> = 1:1:1, WHSV = 180,000 mL g<sup>-1</sup> h<sup>-1</sup>, 1 bar, 200–900 °C.



**Fig. 5.** (a) XRD patterns of spent  $\text{SiO}_2@\text{Ni}$  and spent  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts after dry reforming reaction. (b) TGA of spent  $\text{SiO}_2@\text{Ni}$  and spent  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts after dry reforming reaction. Reaction condition: 20 mL/min of  $\text{CH}_4$ , 20 mL/min of  $\text{CO}_2$ , 20 mL/min of  $\text{N}_2$ , total flow rate = 60 mL/min, 50 mg of catalyst, WHSV = 72,000  $\text{mL g}^{-1} \text{h}^{-1}$ , 1 bar, 700 °C.



**Fig. 6.** (a, b) TEM images and (c–h) EDX mapping of spent  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst after dry reforming reaction. Reaction condition: 20 mL/min of  $\text{CH}_4$ , 20 mL/min of  $\text{CO}_2$ , 20 mL/min of  $\text{N}_2$ , total flow rate = 60 mL/min, 50 mg of catalyst, WHSV = 72,000  $\text{mL g}^{-1} \text{h}^{-1}$ , 1 bar, 700 °C.

carbon deposition on spent catalysts. As shown in Fig. 6, the general morphology of  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst remains almost unchanged after dry reforming reaction, with Ni nanoparticles uniformly dispersed on the surface of  $\text{SiO}_2$  spheres and covered with  $\text{ZrO}_2$  shell. The size of Ni nanoparticles slightly becomes larger as 10 nm. There is no carbon formation observed from EDX mapping of spent  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst, which is consistent with XRD and TGA results. The carbon shown in Fig. 6g is from the carbon film of the copper grid, which is evidenced by comparing Fig. 6a and g. However, large amount of carbon nanotubes appeared around spent  $\text{SiO}_2@\text{Ni}$  catalysts (Fig. 7). The lattice spacing of 0.34 nm is attributed to (002) plane of graphitic carbon (JCPDS 41-1487). From EDX mapping, the catalyst surface, particularly regions with large Ni particles, is covered with carbon deposited during dry reforming reaction. Furthermore, discrete carbon nanotubes are also found, which surround  $\text{SiO}_2@\text{Ni}$  spheres. It is noted that the pressure in the reactor gradually increased during methane dry

reforming over  $\text{Ni}@\text{SiO}_2$  catalyst at 700 °C for 20 h, and the reactor was clogged at the end of reaction test, which is consistent with TGA result of 28% carbon deposition. As the formed carbon nanotubes segregated from the catalysts, which partially explains the unchanged activity of  $\text{SiO}_2@\text{Ni}$  catalyst (Fig. S2). This work aims to utilize the surplus  $\text{CH}_4$  from shale gas and greenhouse gas  $\text{CO}_2$  to produce syngas mixture. The ratio of  $\text{CH}_4$  and  $\text{CO}_2$  could be easily varied by changing the flowrate of each reactants. By using other sources of methane and carbon dioxide such as landfill gas with  $\text{CH}_4$  to  $\text{CO}_2$  ratio higher than 1 [63,64], coking could be more severe comparing to  $\text{CH}_4/\text{CO}_2$  mixture with 1:1 ratio used in this work, due to decomposition of methane to carbon.

The stability of  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst during dry reforming reaction at 700 °C was investigated for 150 h. Shown in Fig. 8, the conversion of  $\text{CH}_4$  at 5 h is 58.7%, which remains almost unchanged as 57.8% at 150 h. For  $\text{CO}_2$ , the initial conversion at 5 h is 58.0%, which slightly reduces to 50.8% at 50 h. After that, the conversion of  $\text{CO}_2$



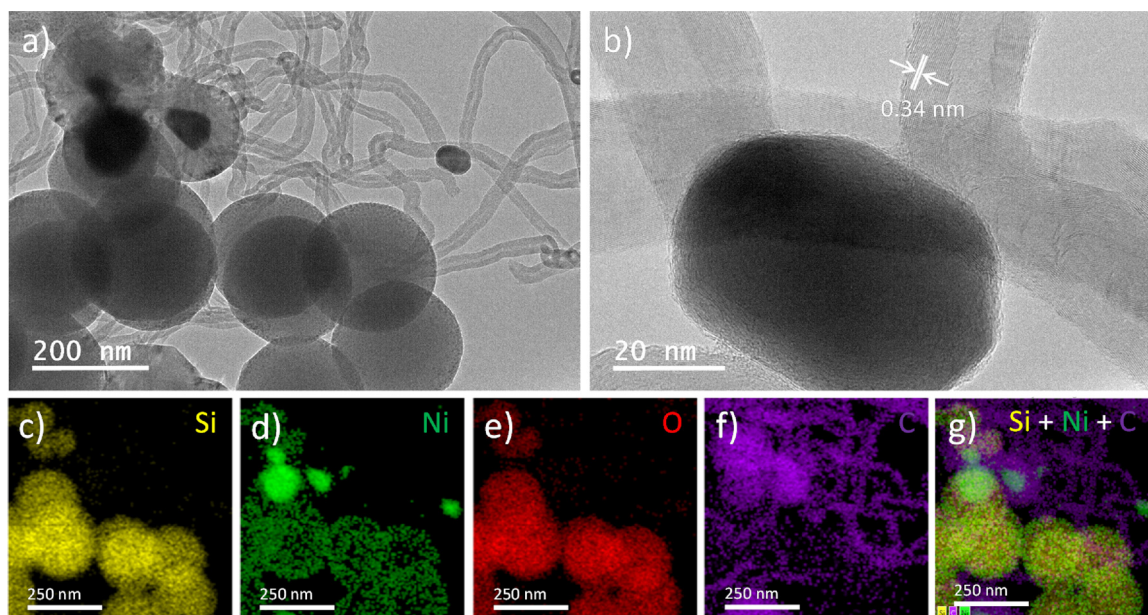


Fig. 7. (a, b) TEM images and (c–h) EDX mapping of spent  $\text{SiO}_2@\text{Ni}$  catalyst after dry reforming reaction. Reaction condition: 20 mL/min of  $\text{CH}_4$ , 20 mL/min of  $\text{CO}_2$ , 20 mL/min of  $\text{N}_2$ , total flow rate = 60 mL/min, 50 mg of catalyst, WHSV =  $72,000 \text{ mL g}^{-1} \text{ h}^{-1}$ , 1 bar,  $700^\circ\text{C}$ .

remains nearly unchanged as 47.7% at reaction time of 150 h.

#### 4.3. In situ X-ray absorption spectroscopy study of $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$ catalyst

The evolution of catalyst structure under reduction and reaction conditions was examined by operando X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure studies of Ni K-edge (Fig. 9). The Ni K-edge XANES spectrum of fresh  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst is similar as that of NiO standard, with an intense white line appearing at 8350.6 eV. The Ni K-edge energy measured at the first inflection point is 8342.3 eV, consistent with that of NiO [65]. Furthermore, a characteristic pre-edge peak is observed at 8332.6 eV in Ni K-edge spectrum, which is attributed to quadrupole  $1s \rightarrow 3d$  transition [66,67]. The  $k^3$ -weighted EXAFS spectrum is presented in Fig. 9c, with curve fitting results shown in Fig. S5 and Table S1. Two major peaks are observed at 2.03 Å and 3.07 Å, which can be assigned to first Ni–O coordination shell and second Ni–Ni coordination shell,

respectively [68,69]. Both of the XANES and EXAFS spectra confirms that the fresh catalyst consists of NiO phase, as the fresh catalyst was prepared via calcination at  $500^\circ\text{C}$  in air. The intensity of the white line decreases with increasing reduction temperature, indicating the reduction process from NiO to Ni. At  $700^\circ\text{C}$ , the intensity of white line decreases significantly and the pre-edge peak at 8332.6 eV disappears, suggesting that NiO is reduced to metallic Ni [70]. As shown in the Fourier transformed EXAFS spectra (Fig. 9c), the peak corresponding to Ni–O coordination disappears. A new peak is observed at 2.47 Å, which is due to first shell Ni–Ni coordination [11,55]. The coordination number (CN) of Ni–Ni is calculated to be  $8.8 \pm 0.8$  based on the best-fit values.

After reduction, the reactor was cooled to  $400^\circ\text{C}$  in  $\text{N}_2$  flow, followed by switching the gas to 5% $\text{CH}_4$ /5% $\text{CO}_2$ /90% $\text{N}_2$ . As shown in Fig. 9b, the Ni K-edge XANES spectrum for  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalyst under reaction condition is similar as that of reduced catalyst. The peak at 2.49 Å is attributed to first shell Ni–Ni coordination (Fig. 9d), with

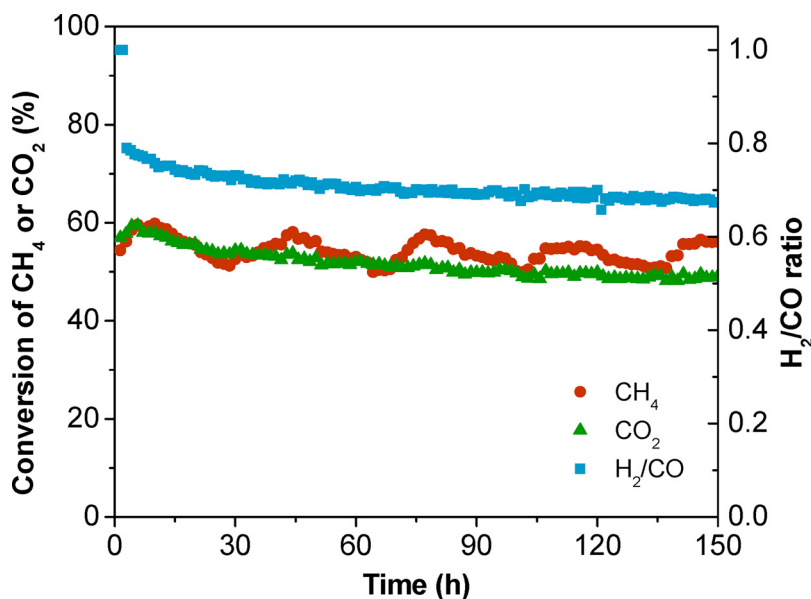
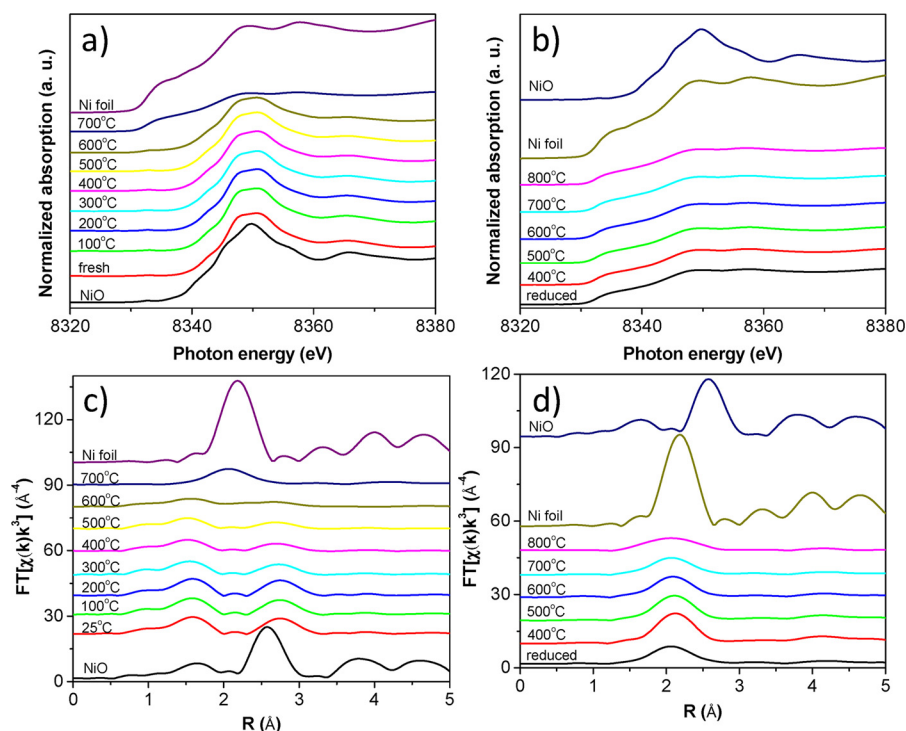
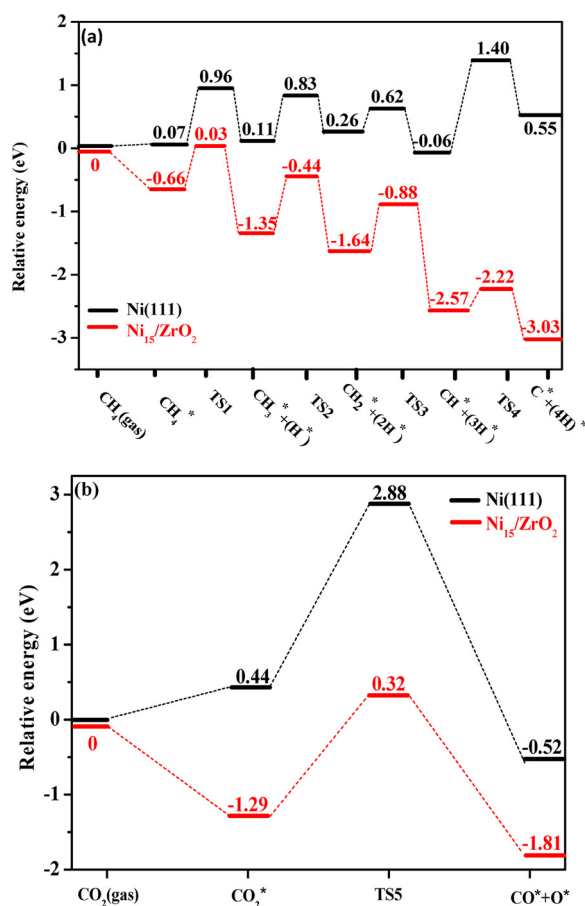


Fig. 8. Stability test of  $\text{SiO}_2@\text{Ni}@\text{ZrO}_2$  catalysts for dry reforming of methane with carbon dioxide. Reaction condition: 10 mL/min of  $\text{CH}_4$ , 10 mL/min of  $\text{CO}_2$ , 10 mL/min of  $\text{N}_2$ , 75 mg of catalyst, WHSV =  $24,000 \text{ mL g}^{-1} \text{ h}^{-1}$ , 1 bar,  $700^\circ\text{C}$ . Red sphere stands for conversion of  $\text{CH}_4$ , green triangle stands for conversion of  $\text{CO}_2$ , and blue square stands for  $\text{H}_2/\text{CO}$  ratio. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).



**Fig. 9.** Operando XANES/EXAFS study of  $\text{SiO}_2\text{@Ni@ZrO}_2$  during (a, c) reduction and (b, d) methane dry reforming. Reduction condition: 1 mg of catalyst + 9 mg of  $\text{SiO}_2$ , 100 mL/min of 3.5%  $\text{H}_2/\text{He}$ , 25–700 °C at 5 °C/min. Reaction condition: 1 mg of catalyst + 9 mg of  $\text{SiO}_2$ , 100 mL/min of 5%  $\text{CH}_4/5\%\text{CO}_2/\text{N}_2$ , 400–800 °C.



**Fig. 10.** The potential energy profiles for (a)  $\text{CH}_4$  sequential dissociation and (b)  $\text{CO}_2$  dissociation on  $\text{Ni}(111)$  and  $\text{Ni}_{15}/\text{ZrO}_2$ , respectively.

the CN of N–Ni as  $9.4 \pm 0.6$ . With increasing the reaction temperature to 800 °C, the XANES and EXAFS spectra remains almost unchanged. At 800 °C, the coordination number of Ni–Ni is  $8.9 \pm 1.0$ , suggesting that the metallic Ni remains also unchanged during dry reforming reaction at 400–800 °C (Fig. S6). It shows that the sandwiched structure of  $\text{SiO}_2\text{@Ni@ZrO}_2$  catalyst is efficient for stabilization of Ni nanoparticles during reaction at high temperature.

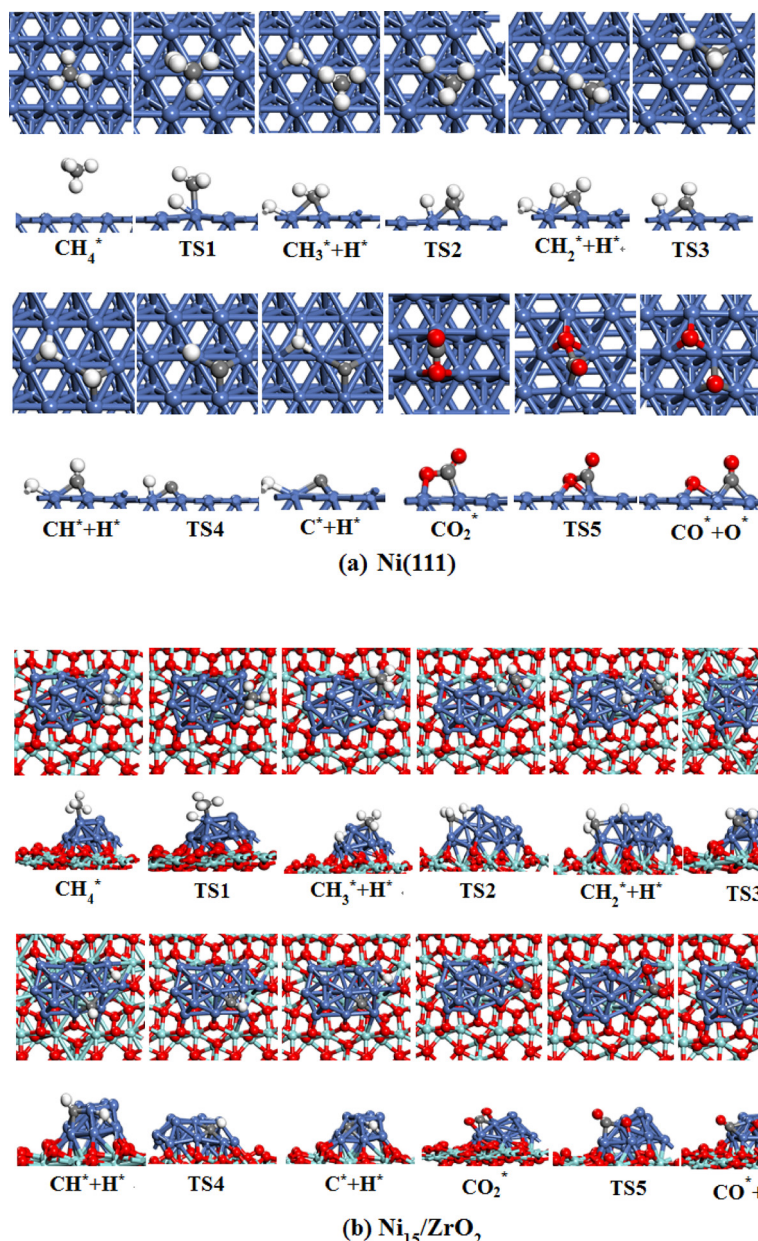
#### 4.4. Reaction pathway on $\text{SiO}_2\text{@Ni}$ and $\text{SiO}_2\text{@Ni@ZrO}_2$ catalysts

Based on XRD, TEM and in-situ XAS studies,  $\text{Ni}(111)$  and  $\text{Ni}_{15}/\text{ZrO}_2$  were selected as model catalysts to represent  $\text{SiO}_2\text{@Ni}$  and  $\text{SiO}_2\text{@Ni@ZrO}_2$ , respectively, for DFT calculations to understand the difference of reaction performance (i.e., activity and coke resistance) for methane dry reforming. Adsorption of reactants  $\text{CH}_4$  and  $\text{CO}_2$ , the intermediates  $\text{CH}_x$  ( $x = 0\text{--}3$ ) and  $\text{CO}$  species in  $\text{CO}_2/\text{CH}_4$  reforming reaction over  $\text{Ni}(111)$  and  $\text{Ni}_{15}/\text{ZrO}_2$  were firstly investigated. The stable geometries of these species are schematically depicted in Fig. S8; the calculated adsorption energies, preferred adsorption sites and corresponding geometric parameters are listed in Table S2. The results show that all these species prefer to be adsorbed at the different sites of  $\text{Ni}_{15}$  cluster rather than the  $\text{ZrO}_2$  and the interfacial site between the Ni particles and the zirconia; in addition, when the species are initially adsorbed at the interfacial site between Ni particles and the zirconia, after geometry optimization, the species migration from the interfacial site to the Ni cluster occurs. Further, all reactions considered in this study showed that the transition state of the reaction also interact with the  $\text{Ni}_{15}$  cluster. Thus, the  $\text{Ni}_{15}$  cluster is the preferred adsorption site for all species and the active center for the reactions instead of the  $\text{ZrO}_2$  and the interfacial site between Ni particles and the zirconia.

##### 4.4.1. $\text{CH}_4$ sequential dissociation on $\text{Ni}(111)$ and $\text{Ni}_{15}/\text{ZrO}_2$

Based on the stable adsorption configurations of the possible species, we then explored  $\text{CH}_4$  dissociation in  $\text{CH}_4/\text{CO}_2$  reforming reaction over  $\text{Ni}(111)$  and  $\text{Ni}_{15}/\text{ZrO}_2$  catalyst, respectively. The calculated dissociation barriers ( $E_a$ ) and reaction energies ( $\Delta E$ ) are listed in Table S3.





**Fig. 11.** The top and side view of the optimized geometries of the reactants, transition states (TS) and products for  $\text{CH}_4$  sequential dissociation and  $\text{CO}_2$  incomplete dissociation (a) Ni(111) and (b)  $\text{Ni}_{15}/\text{ZrO}_2$ , respectively (Ni, Zr, O, C and H atoms in blue, cyan, red, gray and white, respectively) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The corresponding potential energies are shown in Fig. 10, and the structures of the reactant, transition state (TS) and product for the elementary step are presented in Fig. 11.

On Ni(111) surface, the adsorbed  $\text{CH}_4$  dissociates into the co-adsorbed  $\text{CH}_3$  and H species via a transition state (TS1), in which  $\text{CH}_3$  locates at the top site and the dissociating H atom transfers to the hcp site. The C–Ni distance is shortened from 3.459 to 2.058 Å, while the C–H bond length is stretched from 1.097 to 1.605 Å. In the final state,  $\text{CH}_3$  and H species are adsorbed at the fcc and hcp site, respectively. This process overcomes the dissociation barrier of 0.89 eV, and it is neutral in thermodynamics (0.04 eV). The adsorbed  $\text{CH}_3$  further dissociates into  $\text{CH}_2$  and H via TS2, in which the dissociating H atom shifts to the adjacent top site,  $\text{CH}_2$  species adsorbs at the fcc site. The distance between C atoms and H atom is 1.792 Å. In the final state,  $\text{CH}_2$  and H species are adsorbed at the fcc and hcp site, respectively. This reaction is slightly endothermic by 0.15 eV with the dissociation barrier of 0.72 eV. For the sequential dissociation of  $\text{CH}_2$  into CH, followed by its

dissociation into C, in TSs, the breaking-up C–H bond lengths are 1.715 and 1.779 Å for  $\text{CH}_2$  and CH dissociation, respectively. These two reactions have the reaction energies of –0.32 and 0.61 eV with the dissociation barriers of 0.36 and 1.46 eV, respectively.

On  $\text{Ni}_{15}/\text{ZrO}_2$ , the dissociation of adsorbed  $\text{CH}_4$  at the top  $\text{Ni}_1$  site into  $\text{CH}_3$  and H proceeds through TS1, in which both  $\text{CH}_3$  and H species bind to the  $\text{Ni}_1$  atom with the shorter C–Ni bond length of 1.968 Å and the longer C–H bond length of 1.784 Å compared to those (2.251 and 1.111 Å) in adsorbed  $\text{CH}_4$ , respectively. In the final state,  $\text{CH}_3$  and H species transfer to the two adjacent 3-fold hollow sites, respectively. This process is largely exothermic by 0.69 eV with the dissociation barrier of 0.69 eV.  $\text{CH}_3$  can dissociates into  $\text{CH}_2$  and H species via TS2, in which  $\text{CH}_2$  and H species adsorb at the bridge site with the average C–Ni and H–Ni bond lengths of 1.900 and 1.714 Å, respectively; the distance between H atom to C atom is 1.650 Å. In the final state,  $\text{CH}_2$  and H transfer to the two adjacent 3-fold hollow sites, respectively. The dissociation reaction is exothermic by 0.29 eV with the dissociation

barrier of 0.91 eV. For CH<sub>2</sub> dissociation, in TS3, the dissociating H atom binds to the Ni<sub>1</sub>–Ni<sub>11</sub> bridge site with the C–H distance of 1.548 Å, CH species locates at the 3-fold hollow site with the average C–Ni bond length of 1.853 Å. In the final state, H atom transfers to the 3-fold hollow site, and CH transfers to the 4-fold hollow site. The dissociation reaction is exothermic by 0.93 eV with the dissociation barrier of 0.76 eV. For CH species, it dissociates into C and H atom via TS4, in which the C–H bond length is elongated to 1.260 Å. The left C atom remains at the 4-fold hollow site, while the H atom shifts to the adjacent 3-fold hollow site. This step is exothermic by 0.46 eV and overcomes the dissociation barrier of 0.35 eV

#### 4.4.2. CO<sub>2</sub> dissociation on Ni(111) and Ni<sub>15</sub>/ZrO<sub>2</sub>

The dissociation barriers ( $E_a$ ) and reaction energies ( $\Delta E$ ) of CO<sub>2</sub> dissociation over Ni(111) and Ni<sub>15</sub>/ZrO<sub>2</sub> catalyst are listed in Table S3. The corresponding potential energies are shown in Fig. 10; the optimized geometries of the reactants, transition states (TS) and products are illustrated in Fig. 11.

On Ni(111) surface, the adsorbed CO<sub>2</sub> can dissociate into CO and O species via TS5, where the CO species transfer to the adjacent bridge site from the original bridge site while the left O atom migrates to the fcc site with the dissociating C–O distance of 1.592 Å. The average C–Ni and O–Ni bond lengths are 1.978 and 1.974 Å, respectively. In the final state, CO adsorbs at the fcc site and O atom locates the fcc site with the average C–Ni and O–Ni bond length of 1.838 and 1.973 Å, respectively. This reaction has the high dissociation barrier of 2.44 eV, and it is exothermic by 0.96 eV.

On Ni<sub>15</sub>/ZrO<sub>2</sub>, the adsorbed CO<sub>2</sub> dissociates into the adsorbed CO and O species via TS5, in which CO species is adsorbed at the adjacent bridge site with the average C–Ni bond length of 1.867 Å, and the left O species is at the bridge site. Meanwhile, the C–O bond length is stretched from 1.254 to 1.855 Å in TS5. In the final state, CO and O species migrates to the adjacent 3-fold hollow site with the average C–Ni and O–Ni bond length of 1.952 and 1.861 Å, respectively. This step needs to overcome the dissociation barrier of 1.61 eV and it is exothermic by 0.52 eV.

#### 4.4.3. The comparison of CH<sub>4</sub> and CO<sub>2</sub> dissociation between Ni(111) and Ni<sub>15</sub>/ZrO<sub>2</sub>

In order to obtain the effect of the particle size on the catalytic activity, the activity of CH<sub>4</sub>/CO<sub>2</sub> reforming reaction on Ni<sub>15</sub>/ZrO<sub>2</sub> and Ni(111) structure were compared by the highest barrier for CH<sub>4</sub> sequential dissociation and CO<sub>2</sub> dissociation. As shown in Fig. 10, with respect to the gas phase CH<sub>4</sub>, the highest dissociation barrier of CH<sub>4</sub> sequential dissociation into C is only 0.03 eV on Ni<sub>15</sub>/ZrO<sub>2</sub>, which is much lower by 1.37 eV than that (1.40 eV) on Ni(111) surface. The obvious decrease of dissociation barrier indicates that Ni/ZrO<sub>2</sub> catalyst has much higher catalytic activity toward CH<sub>4</sub> dissociation than Ni(111) surface, which well explains the experimental finding that drying reforming activity is improved by 5–7 times after coating with ZrO<sub>2</sub>. On the other hand, for CO<sub>2</sub> dissociation into CO, the larger decrease of 2.56 eV for the highest barrier energy is also found from Ni<sub>15</sub>/ZrO<sub>2</sub> to Ni(111), which also accords with the experimental result that CO<sub>2</sub> conversion is improved after coating with ZrO<sub>2</sub> and further indicates that the activity of Ni<sub>15</sub>/ZrO<sub>2</sub> is obviously superior to the pure metal Ni for CO<sub>2</sub> dissociation. Therefore, Ni<sub>15</sub>/ZrO<sub>2</sub> performs more excellent activity than bulk Ni surface for CH<sub>4</sub>/CO<sub>2</sub> reforming reaction.

Furthermore, we compared the dissociation barriers and reaction energies of the elementary steps for CH<sub>4</sub> sequential dissociation and CO<sub>2</sub> dissociation on Ni<sub>15</sub>/ZrO<sub>2</sub> and Ni(111) to probe into the mechanism of the excellent performance of Ni<sub>15</sub>/ZrO<sub>2</sub>. As shown in Table S3, it can be found that compared to Ni(111) surface, these elementary step releases much more energies for CH<sub>4</sub> sequential dissociation on Ni<sub>15</sub>/ZrO<sub>2</sub>. That is, there is the greater thermodynamic driving force on Ni<sub>15</sub>/ZrO<sub>2</sub> than Ni(111), which are attributed to the obvious enhancement of the adsorption energies of CH<sub>4</sub> and CH<sub>x</sub> (x = 0–3) species on

Ni<sub>15</sub>/ZrO<sub>2</sub> compared to those on Ni(111) surface. On the other hand, for CO<sub>2</sub> dissociation, compared to Ni(111) surface, Ni<sub>15</sub>/ZrO<sub>2</sub> catalyst not only decrease the dissociation barrier (0.83 eV), but also increase the adsorption energy of CO<sub>2</sub>. Namely, the greater thermodynamic and kinetic driving force on Ni<sub>15</sub>/ZrO<sub>2</sub> make CO<sub>2</sub> dissociation more easier compared to Ni(111). In addition, the adsorption energy of CO<sub>2</sub> (–1.29 eV) is much higher than that of CH<sub>4</sub> (–0.66 eV) on Ni<sub>15</sub>/ZrO<sub>2</sub>, leading to catalyst surface enriched with CO<sub>2</sub>; moreover, compared to Ni(111), CO<sub>2</sub> dissociation is more easier on Ni<sub>15</sub>/ZrO<sub>2</sub>, it is inferred that more O atoms from CO<sub>2</sub> dissociation can be obtained to interact with surface C from CH<sub>4</sub> dissociation to inhibit coke formation. On the other hand, the weak adsorption energy of CO<sub>2</sub> (0.44 eV) and CH<sub>4</sub> (0.07) is comparable on bulk Ni, leading to relatively lower CO<sub>2</sub>/CH<sub>4</sub> ratio on bulk Ni surface comparing to that on Ni<sub>15</sub>/ZrO<sub>2</sub> surface, CO<sub>2</sub> dissociation is difficult on bulk Ni surface compared to that on Ni<sub>15</sub>/ZrO<sub>2</sub>, surface C from CH<sub>4</sub> dissociation cannot be effectively eliminated, which may explain the coke formation observed.

## 5. Conclusions

In summary, sandwiched SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst has been developed using wet chemistry synthetic route. The porous ZrO<sub>2</sub> shell is essential for uniform dispersion and stabilization of 6 nm Ni nanoparticles in-between SiO<sub>2</sub> core and porous ZrO<sub>2</sub> shell. Without ZrO<sub>2</sub> coating, large Ni particles with size of 33 nm are formed on the surface of silica spheres. The ZrO<sub>2</sub> coated SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst exhibited excellent activity for methane dry reforming, with its activity 5–7 times higher than that of uncoated SiO<sub>2</sub>@Ni catalyst at 500–700 °C. In addition, the SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst is coke resistant, and very robust for extended reaction time. Operando XAS studies confirms SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst having metallic Ni phase under dry reforming reaction condition at 500–800 °C. Density functional theory (DFT) calculations suggest that Ni<sub>15</sub>/ZrO<sub>2</sub> not only reduce CO<sub>2</sub> dissociation barrier, but also effectively stabilize the reactants and the intermediates involving in CH<sub>4</sub>/CO<sub>2</sub> reforming reaction, such as CH<sub>4</sub>, CO<sub>2</sub>, CH<sub>x</sub> (x = 0–3) and CO; as a result, Ni<sub>15</sub>/ZrO<sub>2</sub> significantly reduces highest dissociation barrier of CH<sub>4</sub> and CO<sub>2</sub> and improve the catalytic activity for CH<sub>4</sub>/CO<sub>2</sub> reforming reaction. Furthermore, the higher adsorption energy of CO<sub>2</sub> comparing to CH<sub>4</sub> and the lower dissociation barrier of CO<sub>2</sub> on SiO<sub>2</sub>@Ni@ZrO<sub>2</sub> catalyst explains its coke resistance during methane dry reforming reaction.

## Conflict of interest

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.05.021>.

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